

# Chapter 15

## Development of $\text{LiCoO}_2$ Used for Rechargeable Lithium-Ion Battery

Hidekazu Awano

### 15.1 Introduction

Currently, the lithium-ion battery is an indispensable battery for the power sources of mobile devices such as notebook-sized personal computers and mobile phones since the rechargeable lithium-ion battery was commercialized for the first time in 1990. In particular, the rechargeable lithium-ion battery and the mobile phone have both expanded their markets. The rechargeable lithium-ion battery has become widely used in the Asian countries in connection with the popularization of mobile phones in South Korea and China. The performance of the rechargeable lithium-ion battery (in particular, capacity) is improved every year. Initially, the number of manufacturers of rechargeable lithium-ion batteries was as high as 10–11 companies in Japan, including newcomer companies, while the number in China has not been accurately counted. On the other hand, the battery price is continuously decreasing. Currently, some manufacturers plan to withdraw from the rechargeable lithium-ion battery business, and there is the possibility that the existing manufacturers might be consolidated into a few companies in the near future. The manufacturing of a battery is not easily accomplished just by introducing new equipment; advanced know-how is required for its manufacturing. Therefore, it is assumed that the Japanese manufacturers still dominate the overseas manufacturers in this field. Moreover, when we pay attention to other energy devices, the developments of the capacitor and the fuel cell are also proceeding, and it is expected that they will compete or coexist with the rechargeable lithium-ion battery in the future. Nippon Chemical Industrial Co. Ltd., also is involved in the development so that we can survive as a supplier of the positive electrode-active material in the future.

In this chapter, we will introduce the manufacturing process and the characteristics of  $\text{LiCoO}_2$ , which is mainly used as the positive electrode-active material of

---

H. Awano

Nippon Chemical Industrial Co., Ltd., 9-11-1, Kameido, Koto-ku Tokyo 136-8515, Japan  
hidekazu.awano@nippon-chem.co.jp

the rechargeable lithium-ion battery. However, some technologies are confidential; therefore, we would like to ask you to overlook this area if not easily understood.

### 15.1.1 Background of Development

Nippon Chemical Industrial Co., Ltd. has been manufacturing and selling lithium salts at its establishment. The names of the products and their uses are listed in Table 15.1.  $\text{LiCoO}_2$ , which is used for the positive electrode-active material of the rechargeable lithium-ion battery, was selected in order to place a lithium salt product with a high additional value on the market. Its development began in 1991. The supply of samples to battery manufacturers began in 1992. The initial evaluation by the customer was finished in 1993, and several tens to hundreds of kilograms of product were experimentally manufactured using a pilot plant. The maximum production of 2 tons/month was recorded in 1994. The design of the mass production plant was started at the same time, and the mass production plant of 20 tons/month was set up in 1995. Afterward, the capacity of the plant was increased many times since then.

### 15.1.2 Why is $\text{LiCoO}_2$ Used?

As described in the first paragraph,  $\text{LiCoO}_2$  is used mainly for the positive electrode-active material of the present rechargeable lithium-ion batteries. In the early stage of its development, it was expected that  $\text{LiCoO}_2$  had problems with price and the resource of cobalt, and would soon be substituted by nickel-type or manganese-type material. Even in presentations in the journals, conferences, and so forth, at that time, examples of studying  $\text{LiCoO}_2$  were few, although the development of the nickel-type and manganese-type were active. However, in actuality, the commercial rechargeable lithium-ion batteries using the nickel-type or the manganese-type material are still limited. Table 15.2 shows the features of each material. It can be understood that  $\text{LiCoO}_2$  is a material that excels in the balance of the capacity,

**Table 15.1** Lithium salts manufactured by Nippon Chemical Industrial Co., Ltd

Salt	Use
Lithium carbonate	Battery material; special glass
Lithium hydroxide	For carbon dioxide absorbent and grease
Lithium chloride	Aluminum welding material; humidity control material
Lithium bromide	For freezer and air conditioner
Lithium phosphate	Electronic and electric material
Lithium nitrate	Electronic and electric material

**Table 15.2** Features of commercial rechargeable lithium-ion batteries

Material	Capacity <sup>a</sup>	Rate	High temp.	Safety	Cost	Process
$\text{LiCoO}_2$	B	B	B	B	C-B	A
$\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$	A	C	B	C	B	C
$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$	B	C	C	B	B	B
$\text{LiMn}_2\text{O}_4$	C	C	C	A	B	C

<sup>a</sup> A excellent, B good, C fair



CAS No.12190-79-3  
 Melting point: 1100°C or more  
 True specific gravity: 5.1  
 Particle size: 2-50μm  
 Specific surface area: 0.1-1.0m<sup>2</sup>/g  
 Tap density: 1.5-3.0

**Fig. 15.1**  $\text{LiCoO}_2$  powder

rate characteristics, cycling characteristics, high/low temperature characteristics, safety, and so on, when the battery characteristics of the rechargeable lithium-ion batteries are considered. Moreover, the manufacturing of  $\text{LiCoO}_2$  can be carried out easily by mixing cobalt oxide with a lithium salt in a certain ratio and baking it at 700°C or more, as will be described later. Thus, the simplicity of its manufacturing process is considered to be one of the reasons why  $\text{LiCoO}_2$  is used for the positive electrode-active material of rechargeable lithium-ion batteries.

### 15.1.3 Physical Properties of $\text{LiCoO}_2$

The main physical properties of  $\text{LiCoO}_2$  are indicated in the following section (mainly for the  $\text{LiCoO}_2$  manufactured by our company). A photograph of  $\text{LiCoO}_2$  is shown in Fig. 15.1.

### 15.1.4 Resource and Price of Cobalt

In the past, cobalt generally has been recognized as an expensive raw material. The reason for this is that the cobalt is a speculation commodity, and its price always changes. Figure 15.2 shows the changes in the market price of cobalt since 1997. Thus, a very large change is observed. The price fell below \$7 in April, 2002. (It is generally said that if the price becomes below \$10, it does not pay the mining costs at the mine.) Afterward, it gradually increased, then rapidly increased to \$28 in November, 2003. A possible reason for this increase is an increase in the amount of  $\text{LiCoO}_2$  used for the positive electrode-active material because the rechargeable lithium-ion battery market is expanding quite rapidly. Moreover, as another reason for this increase, an increase in the concern of cobalt raw material also can be considered because each battery manufacturer announced his policy to expand the production volume of the rechargeable lithium-ion battery one after another. (The effect of the speculator is one of these factors.) Therefore, the battery manufacturers could not help raising the price of a cell by 8–10%. However, the transfer to the cell price does not appear to be occurring.

The Congo, Zambia, Canada, Morocco, and New Caledonia are considered the main places of production of the cobalt ore. The main use of the cobalt ore was for aircraft superalloys, hard metal tools, magnets, catalysts, and pigments before the rechargeable lithium-ion battery was developed. Therefore, the cobalt oxide that could be used for batteries was low. However, the number of manufacturers producing the cobalt oxide recently has increased due to the expansion of the market. In our company, various cobalt raw materials produced by 6–7 companies are always being evaluated.

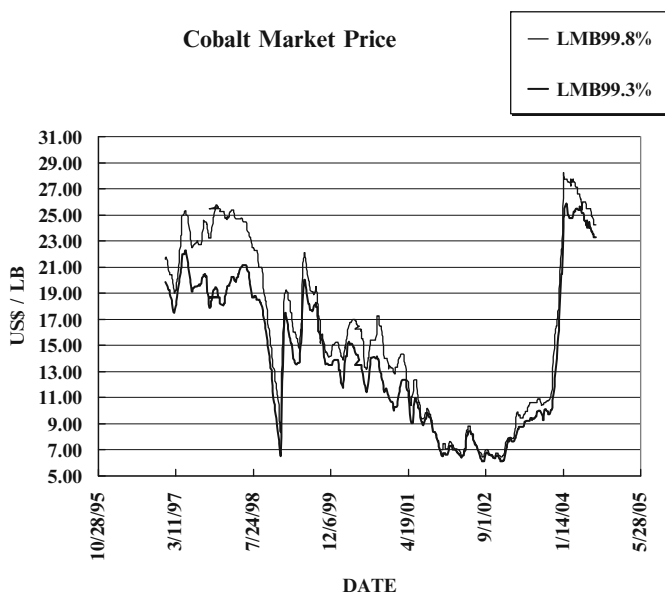


Fig. 15.2 Price fluctuation of cobalt

### 15.1.5 Trend of $\text{LiCoO}_2$ in the Future

Presently, the market price of cobalt is high; therefore, the application of  $\text{LiCoO}_2$  to the positive electrode active material is depressed, and it is shifting to the nickel-type, manganese-type, and iron-type materials. However, it is expected that the price will settle to a certain level because a new cobalt project is scheduled to start after 2007. Moreover, it is considered that it will not become zero in volume because it is a material widely acknowledged in the market as a positive electrode-active material for rechargeable lithium-ion batteries. Furthermore, although mobile devices such as mobile phones and notebook-sized personal computers were the principal uses of the rechargeable lithium-ion battery, it is expected that the market for new uses (for power tools using a medium- to large-sized battery) will expand in the future. However, it is necessary to continue the effort to decrease the price of the material and to improve its characteristics. It is considered that there still remains enough room for improvement in the characteristics of  $\text{LiCoO}_2$ , and is described in detail in Chap. 3.

## 15.2 Manufacturing Method and Quality of $\text{LiCoO}_2$

Various synthesis methods were proposed at the beginning of development of the lithium-ion secondary battery. It is understood that the  $\text{LiCoO}_2$  is obtained using a cobalt compound and a lithium compound as the raw materials and synthesizing it by heating as shown in Table 15.3. It is postulated that cobalt carbonate was first used as the cobalt compound. After large-scale production started, cobalt oxide ( $\text{Co}_3\text{O}_4$ ) as the cobalt compound, and lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) as the lithium compound began to be mainly used due to the stability of their quality and supply,

**Table 15.3** Examples of synthesis method of  $\text{LiCoO}_2$

References	Synthesis method
Mizushima et al. <sup>1</sup>	Pellets consisting of a mixture of lithium carbonate and cobalt carbonate were calcined and then heat-treated at 900°C in air for 20 h. As a result of the analysis, the composition was assumed to be $\text{Li}_{0.99}\text{Co}_{1.01}\text{O}_2$
Molenda et al. <sup>2</sup>	Stoichiometric quantities of lithium carbonate and cobalt oxide were mixed and pressed into a pellet of 0.8-cm diameter, 0.1-cm high. It was heated at 1,170 K for 4 days
Reimer et al. <sup>3</sup>	Stoichiometric quantities of $\text{LiOH}\cdot\text{H}_2\text{O}$ and $\text{CoCO}_3$ were heated in air at 850°C
Gummow et al. <sup>4</sup>	The product ( $\text{LT-LiCoO}_2$ ) synthesized in low temperature (400°C) exhibited low crystallinity and was more stable in the electrolyte compared to the product synthesized at high temperature (900°C)
Ohzuku et al. <sup>5</sup>	Stoichiometric quantities of $\text{Li}_2\text{CO}_3$ and $\text{CoCO}_3$ were calcined at 650°C in air for 12 h and then heat-treated at 850°C for 24 h
Gupta et al. <sup>6</sup>	$\text{Li}_2\text{CO}_3$ and $\text{Co}_3\text{O}_4$ were calcined at 550°C in air for 5 h, and then heat-treated at 850°C for 24 h

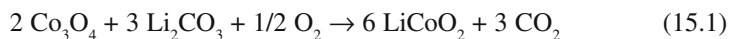
**Table 15.4** Features of typical synthetic reaction of cobalt compound and lithium carbonate

	Co content (%)	Required amount (g) for synthesizing 1 kg of LiCoO <sub>2</sub>		Reaction by-product (g) for synthesizing 1 kg of LiCoO <sub>2</sub>		Preservation stability <sup>a</sup>
		Co salt	Li <sub>2</sub> CO <sub>3</sub>	CO <sub>2</sub>	H <sub>2</sub> O	
Cobalt oxide	73	820	380	225	–	B
Cobalt carbonate	49	1,220	380	675	–	D
Cobalt hydroxide	63	950	380	225	180	C

<sup>a</sup> B good, C fair, D bad

the easiness of handling, and so forth. Table 15.4 shows the features of the typical synthesizing reactions between the cobalt compound and the lithium carbonate. It can be understood that Co<sub>3</sub>O<sub>4</sub>, which produces fewer reaction by-products, is advantageous.

The reaction scheme for the LiCoO<sub>2</sub> is indicated by the following equation. It is a simple process:



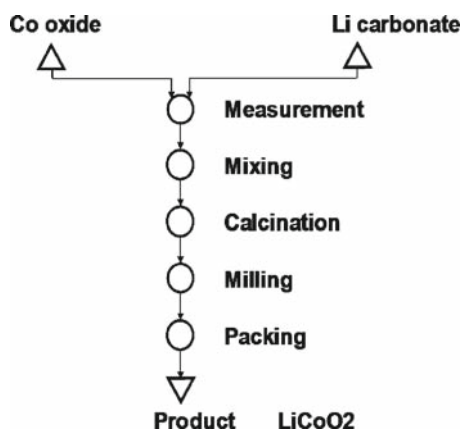
Moreover, although the reaction of the cobalt oxide and the lithium carbonate is fundamental, it also is possible to synthesize LiCoO<sub>2</sub> by combining other cobalt salts and lithium salts. Formerly, it was possible to supply one grade of material to the customers of two to three companies. However, because other materials (electrolytic solution, electrolyte, negative electrode-active material, etc.), which are used in the rechargeable lithium-ion battery, are different and the required battery characteristics are different, we are now supplying a specific grade material for each customer or a specific grade material for each kind of battery (polymer type, rectangular type, and cylindrical type). Recently, a demand from our customers to improve the characteristics and to stabilize the quality has been gradually increasing.

### 15.2.1 Manufacturing Method

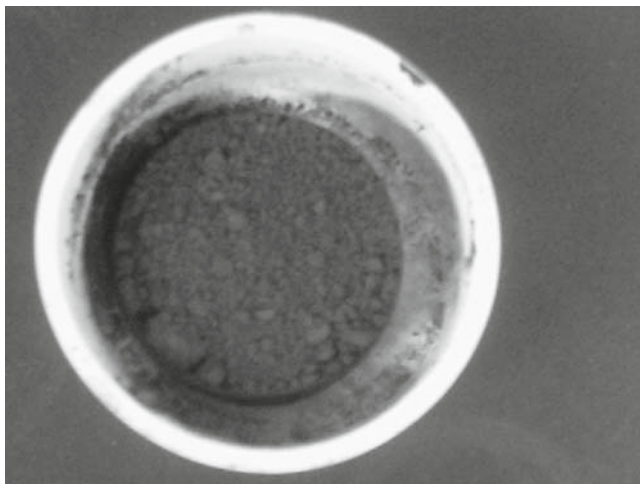
Figure 15.3 shows a flowchart of the manufacturing process of lithium cobaltate. As is understood from the flowchart, after mixing the cobalt oxide and the lithium carbonate at a certain Li/Co ratio, the mixture is baked. After it is baked, it becomes a block as shown in Fig. 15.4, so it is crushed and then packaged as a product. Hereafter, the most important point of each manufacturing process will be introduced.

#### 15.2.1.1 Mixing Ratio

The molar ratio of lithium and cobalt is very important to the manufacturing of LiCoO<sub>2</sub>. The particle size and the battery characteristics are significantly influenced



**Fig. 15.3** Flowchart of manufacturing process of  $\text{LiCoO}_2$



**Fig. 15.4** Baked block

by changing the molar ratio. Therefore, it is a very important control point in the manufacturing process. In order to control this molar ratio within a predetermined range, controlling the purity of the lithium carbonate and the cobalt oxide raw materials is definitely required and also to accurately measure the weight of the raw materials. Moreover, it is important that the raw materials are accurately measured, and the entire quantity is placed in the mixer. When a strongly adhesive raw material is used, deviation in the blended charges from the predetermined rate might occur due to material remaining in the piping. This trouble is liable to be accidentally overlooked during examination in the laboratory.

### 15.2.1.2 Mixing Method

In the mixing process, it is important to uniformly mix the raw materials, which have been accurately measured. There are roughly two methods, i.e., the wet type and dry type. Generally, it seems that many manufacturers are adopting the dry type mixing for manufacturing  $\text{LiCoO}_2$ . An important point is that these two raw materials are uniformly mixed when using the dry process. The uniformity of the mixing is dependent on the kind of mixer. The selection of the mixer is based on the know-how of each company, although the details of the kind of mixer should be found in the manufacturer's literature. Moreover, the particle size, apparent density, and so forth of the lithium carbonate and cobalt oxide influence the homogeneity of the mixing state. Therefore, when the raw material is changed, it is important to optimize the mixing time, rotation speed, and so on. If the homogeneity worsens, the difference in a lot increases, the fraction of unreacted cobalt oxide and lithium carbonate increases, and the battery characteristics and so forth are negatively affected.

### 15.2.1.3 Baking Method

The blended charges are then baked in the baking furnace. This baking process significantly affects the quality of  $\text{LiCoO}_2$ . In particular, oxygen is consumed and carbon dioxide is released during the synthetic reaction as understood from the reaction equation. It is important to establish a baking method in which the supply of oxygen and discharge of carbon dioxide can be smoothly carried out. When running our study while considering this respect, it is necessary to select an electric furnace or gas furnace and to determine the firing atmosphere, firing time, and temperature rise pattern.<sup>7</sup> Moreover, various conditions also should be determined that include the kind of baking tray to be used for baking the blended charges, the amount of blended charges to be charged, and the thickness of the charging of the blended charges. In order to control the quality of the products, it becomes an important point as to how to control these points. The scanning electron microscopy (SEM) images of  $\text{LiCoO}_2$  in various firing atmospheres are shown in Fig. 15.5 (under the conditions of the same firing temperature and Li/Co ratio).

It can be understood that the physical properties of  $\text{LiCoO}_2$  changed depending on the baking atmosphere. The amount of charging of the blended charges also affects the quality of the  $\text{LiCoO}_2$ , although its effect is not remarkable as that of the baking atmosphere.

### 15.2.1.4 Milling

After baking, it becomes a lump as described in Sect. 15.2.1. It is necessary to mill this lump into particles of a certain size (in some cases, depending on the manufacturing method or the manufacturing condition, it might not become a lump). For  $\text{LiCoO}_2$ , strictly speaking, the expression "crushing" might be better than "milling." A typical SEM photograph of our  $\text{LiCoO}_2$  is shown in Fig. 15.6.

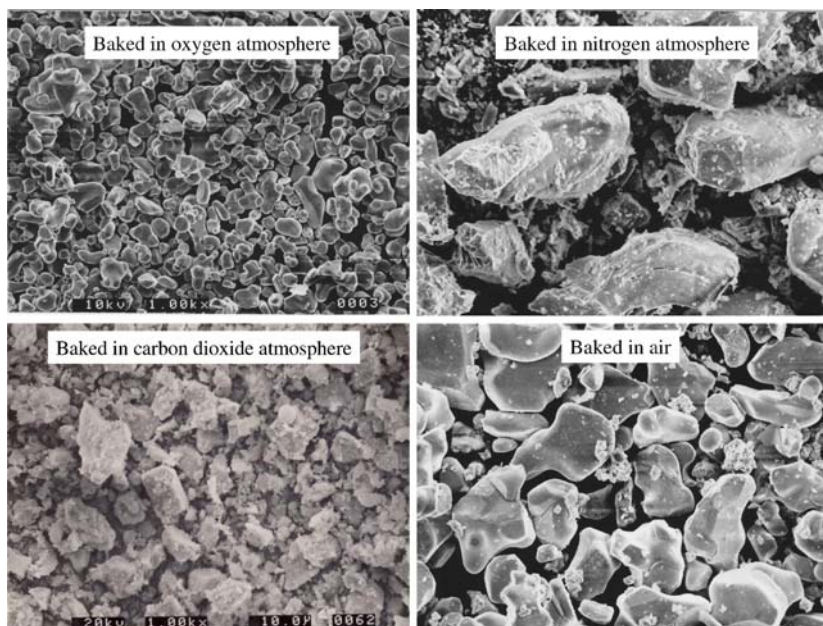


Fig. 15.5 Baking of  $\text{LiCoO}_2$  in various atmospheres

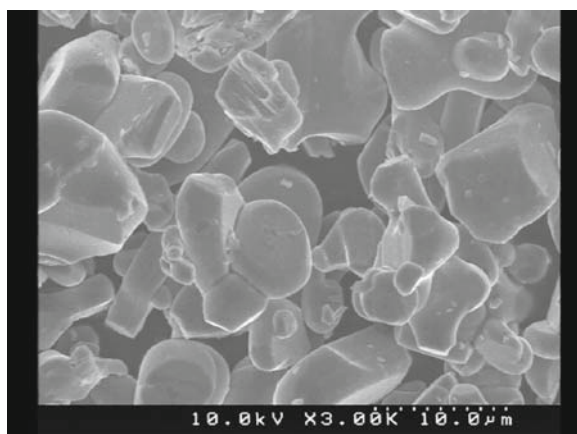


Fig. 15.6 SEM photograph of  $\text{LiCoO}_2$

During the milling process of our  $\text{LiCoO}_2$ , we do not mill the primary particle. It is confirmed in our test results that with excessive milling, which mills the primary particles, the number of fine powder particles increases and the battery characteristics, such as the charge and discharge cycle characteristics and so forth, deteriorate. Therefore, selection of the mill and optimization of the milling conditions are required.

### 15.2.2 *Qualities*

The physical properties listed in the following section are mainly enumerated as the quality of  $\text{LiCoO}_2$ :

- Average particle size, particle size distribution
- Specific surface area
- Water content
- Tap density
- Residual lithium content
- Crystallinity
- Particle shape
- Amount of impurities

All these items are assumed to influence the battery characteristics. Therefore, it recently has become important in manufacturing to stabilize these qualities. In order to stabilize these qualities, it is important to know how to control each manufacturing process as described in Section 2.1. In the following section, we will go into detail about the qualities, which are regarded as especially important.

#### 15.2.2.1 Water Content

The battery characteristic deteriorates when the rechargeable lithium-ion battery is contaminated with water. Naturally, it is desired that the water content in  $\text{LiCoO}_2$  used as the positive electrode-active material be controlled below a certain value. Moreover, currently a further decrease in the water content level is demanded by our customers. Although it may be considered that there is no problem because there is a process to make a slurry of the positive electrode-active material and to dry it, it is known that the water in  $\text{LiCoO}_2$  consists of both physical adsorption and chemisorptions.<sup>8</sup> Because the water, which has been chemically adsorbed, cannot be removed during this drying temperature, it is important to stop the inclusion of moisture from the manufacturing process.

#### 15.2.2.2 Residual Alkali

The lithium carbonate used as the raw material is alkaline. Basically, the ratio of Li/Co is 1. However, in our company, there are some grades where the lithium carbonate remains in the  $\text{LiCoO}_2$  because they are baked using a blended charge having a composition with a slight excess of lithium. If the alkali remains in the product, there is a possibility of problems such that the viscosity of the slurry of the positive electrode-active material increases or the slurry becomes gelled [polyvinylidene fluoride (PVDF) is polymerized].<sup>9</sup> During the early stage of  $\text{LiCoO}_2$  manufacturing, this problem frequently happened in the process of making the slurry. Moreover, it was reported that the content of silicon also is important for the effect

of the residual alkali.<sup>10</sup> At present, a check of the alkali is carried out in the process and the quality problem such as gelation of the electrode slurry has not occurred.

### 15.2.2.3 Specific Surface Area

The specific surface area has a close relationship with the particle size described in the next paragraph. The surface is a place where the reaction with electrolyte occurs and the stabilization of the quality is desired. Our  $\text{LiCoO}_2$  has a surface smoothness feature.<sup>11</sup>

### 15.2.2.4 Particle Size

The particle size control is a very important item for the quality of  $\text{LiCoO}_2$  in our company. In general, the particle size distribution of our  $\text{LiCoO}_2$  has a sharp peak<sup>12</sup>; however, an attempt to improve the performance by adjusting the particle size distribution also is being performed (described in Section 3.1). Our  $\text{LiCoO}_2$  is being evaluated in the market as having a high safety for the rechargeable lithium-ion battery-positive electrode by controlling the particle size distribution and the particle shape.

### 15.2.2.5 Impurities

During the early stage of the development of  $\text{LiCoO}_2$ , we used materials that were as pure as possible. However, there is still room to examine what level of purity is required. Examination of the impurity level is required in order to decrease the price of  $\text{LiCoO}_2$  in the future. However, it is important that metal impurities should be as low as possible. It is necessary to pay close attention to any contamination from the raw materials and contamination from the manufacturing facilities. Many metal parts are used in the manufacturing facilities of cobalt oxide as the raw material and  $\text{LiCoO}_2$ . The contamination from the process due to the wearing of the metal parts may cause an internal short circuit of the battery. In particular,  $\text{LiCoO}_2$  has a high hardness and there is a significant possibility of wearing down the mill and transport facilities. The hardness of  $\text{LiCoO}_2$ , which was assumed by comparing the result of the pushing hardness measured by the micro-Vickers hardness test method with the correlation chart of Mohs hardness,<sup>13</sup> corresponds to 6–8 of Mohs hardness (cf Fig. 15.7b). It is almost the same hardness as that of quartz (Mohs hardness = 7). Consequently, it is important for manufacturing facilities to take measures against the wearing down of the metals. At present, a battery system of 2,000 mAh or more is the major design for the 18650 type and production of higher capacities, which is more than twice that of the early stages, is occurring. In order to secure the quality of batteries, decreasing the amounts of metal impurities as the capacity increases is required.

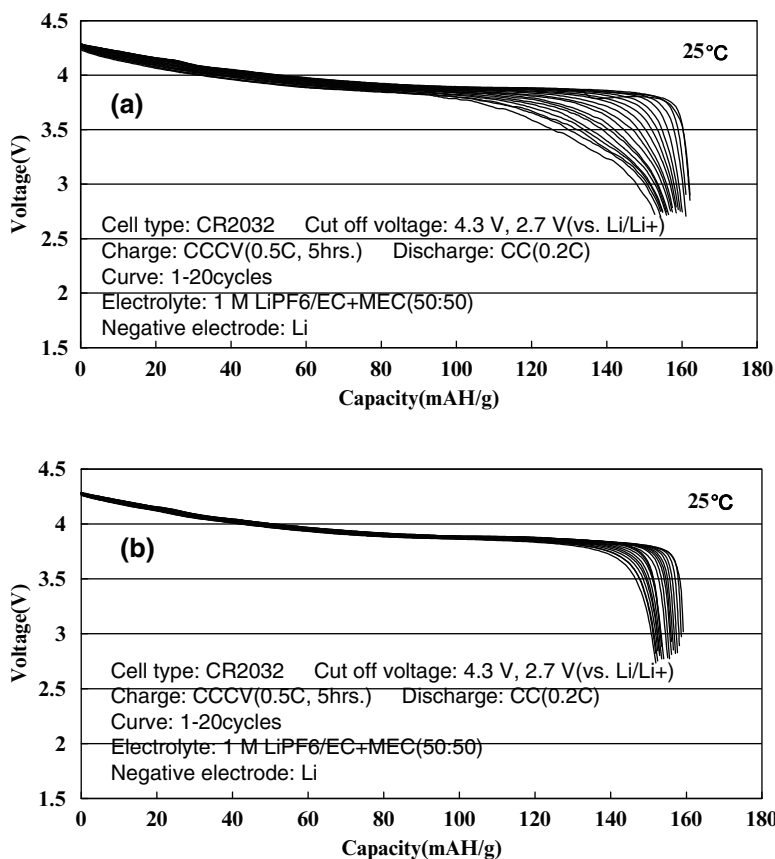


Fig. 15.7 (a) Cobalt oxide A and (b) cobalt oxide B

## 15.3 Further Improvement in the Characteristics of LiCoO<sub>2</sub>

### 15.3.1 Particle Size Control

The shapes, the mean particle size, and the specific surface area of LiCoO<sub>2</sub> can be controlled by optimizing the mixing ratio, the mixing method, the baking method, and the milling conditions. The control of the particle size is comparatively easy compared with other nickel-type and manganese-type materials. Because LiCoO<sub>2</sub> is comparatively stable at high temperature (700–1,000°C), and when it is baked at high temperature the particle grows due to the sintering, a particle of any size can

be obtained. On the other hand, for  $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$ , the temperature range where they are stable is narrower than that of  $\text{LiCoO}_2$ , and its grain growth cannot be easily performed. Therefore, the adjustments of the  $\text{MnO}_2$  and co-precipitated hydroxide, which is the raw material of  $\text{NiMnCo}$ , are required. This easiness in treating might be one of the reasons why  $\text{LiCoO}_2$  is favored. As described above, because the particle size and the specific surface area significantly affect the cell characteristics, their control is important.

### 15.3.2 Selection of Raw Material

As mentioned above, lithium carbonate is used as the raw material for lithium, and cobalt oxide is mainly used as the raw material for cobalt. However, there are many kinds of lithium carbonates and cobalt oxides, which have various powder properties. The characteristics of the synthesized  $\text{LiCoO}_2$  is significantly different depending on the mean particle size, the liability to flocculate, and the impurities as shown in the example below. The examples are shown in Fig. 15.7. It can be understood that the two kinds of  $\text{LiCoO}_2$ , which have similar physical properties, exhibit different charge-discharge cycle characteristics.

### 15.3.3 Control of Impurities

There is an example where additives are positively used in order to satisfy the various needs of the battery characteristics at present. Many methods have been reported. They include methods to substitute another element (Ni, B, Al, etc.) for the cobalt site in order to reduce the change in the crystal lattice due to the occlusion and evolution of lithium,<sup>13–16</sup> and a method to substitute iron in order to reduce the cost.<sup>17</sup>

At present, various additives have been evaluated; however, some elements remarkably decreased the electric capacity. It is important to balance the kind and amount of additives, otherwise the total performance might decrease. On the other hand, the product quality might be negatively affected by other impurities. Because almost no contamination of impurities comes from the manufacturing process, controlling the raw material is important.

### 15.3.4 Surface Treatment

For the lithium-ion battery-positive electrode used for a high oxidation potential, it is considered that the control of the surface conditions will become the main point of development in the future. Recently, many attempts to improve the surface

conditions of the lithium-ion battery electrode were carried out. A surface coating with an electric conductive material in order to improve the electric conductivity<sup>18</sup> and an improvement in the cycling characteristics by coating the oxide with  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and  $\text{MgO}$  on the surface have been reported.<sup>19</sup> It is reported that a big difference was obtained when the cycle test was carried out under the conditions of the high potential of 4.5 V,<sup>20</sup> although no difference occurred with a low potential (4.2 V vs.  $\text{Li/Li}^+$ ). In connection with this phenomenon, there is a report suggesting that the cycling capability and the elution of cobalt into the electrolyte in the form of  $\text{Co}^{4+}$  can be correlated when the charging and discharging are repeated.<sup>21</sup> It will be important for the development in the future to know how to prevent these phenomena by surface modification and structure modification.

### ***15.3.5 Producing Higher Capacity (Higher Density, Higher Voltage, Nickel-Type Material)***

When the method for developing a higher capacity is discussed, the existence of the nickel-type material cannot be disregarded. The possibility of the nickel-type material had been discussed already before the lithium-ion battery was commercialized. Although the nickel-type material is being used for some batteries on the market, the amount being used is not very significant to replace  $\text{LiCoO}_2$  yet. It appears to be a reality that the various characteristics, such as safety, residual lithium on the surface, and low electrical discharge potential, which have been discussed, have not yet been solved completely. The merits of  $\text{LiCoO}_2$  are superior to those of the nickel-type material when considering the balance of the battery characteristics, even if there are some improved characteristics for the nickel-type. Therefore, it will be important to improve  $\text{LiCoO}_2$  by making the material more attractive. When the method to increase the capacity of  $\text{LiCoO}_2$  is considered, it seems that increasing the density of the electrode and the extent of raising the working voltage are the main problems. However, these two requirements are trade-offs. For instance, it is known that if the particle size is increased in order to increase the electrode density, the charging/discharging rate characteristics and the cycling characteristics become inferior, and if the operating voltage is increased, the safety and the cycling characteristics become insufficient although a high capacity is obtained. Therefore, the technology, which improves the total performance such as the cycling characteristics, the charging/discharging rate characteristics, the safety, and so forth, is required in order to obtain a high capacity.

## **15.4 Conclusion**

With respect to  $\text{LiCoO}_2$  of the positive electrode-active material for the lithium-ion secondary battery, some of the technological changes have been described. It is said that the improvement in the capacity of the lithium-ion secondary battery based on

the positive electrode material is not proceeding as quickly compared with the improvements in negative electrode material. A significant reason is that an appropriate material that has a good balance, which can be used as a replacement of  $\text{LiCoO}_2$ , has not been found. However, a sudden rise in the cobalt price occurred in recent years, and the examination of  $\text{LiNi}_{1-x-y}\text{Mn}_y(\text{or Al}_y)\text{Co}_x\text{O}_2$ ,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ , and  $\text{LiMn}_2\text{O}_4$  is becoming active again as alternative materials. Although it is considered that these new electrode materials will take the place of  $\text{LiCoO}_2$  in the future, the fact that  $\text{LiCoO}_2$  is quantitatively dominating the market will be unchanged for a while.

## References

1. Mizushima et al., *Mater. Res. Bull.*, **15**, 783 (1980).
2. J. Molenda et al., *Solid State Ionics*, **36**, 53 (1989).
3. J.N. Reimers et al., *J. Electrochem. Soc.*, **139**, 2091 (1992).
4. R.J. Gummow et al., *Mater. Res. Bull.*, **27**, 327 (1992).
5. T. Ohzuku et al., *J. Electrochem. Soc.*, **141**, 2972 (1994).
6. R. Gupta et al., *J. Solid State Chem.*, **121**, 483 (1996).
7. N. Yamazaki, K. Negishi, Japanese Examined Patent Application Publication NO.3274016.
8. N. Yamazaki, K. Negishi, H. Awano, Japanese Unexamined Patent Application Publication NO. 10-334919.
9. N. Yamazaki, K. Negishi, M. Kikuchi, Japanese Unexamined Patent Application Publication NO. 10-64518.
10. N. Yamazaki, H. Awano, K. Negishi, Japanese Unexamined Patent Application Publication NO. 11-162465.
11. N. Yamazaki, H. Awano, K. Negishi, Japanese Unexamined Patent Application Publication NO. 11-125325.
12. N. Yamazaki, K. Negishi, Japanese Examined Patent Application Publication NO. 3396076.
13. H. Tsukamoto et al., *J. Electrochem. Soc.*, **144**, 3164 (1997).
14. S. Levasseur et al., *Solid State Ionics*, **128**, 11 (2000).
15. T. Ohzuku, M. Kouguchi et al., The 35th Battery Symposium in Japan Abstract, 2C01, P129 (1994).
16. H. Mishima et al., The 35th Battery Symposium in Japan Abstract, 3C06, 175 (1994).
17. H. Tacbuchi et al., The 40th Battery Symposium in Japan Abstract, 1C02, 231 (1999).
18. M. Kadowaki et al., The 42th Battery Symposium in Japan Abstract, 1A01, 86 (2001).
19. G.T. Fey et al., IMLB 12th Meeting, Abstract No. 36 (2000).
20. H. Kurita et al., The 44th Battery Symposium in Japan, Abstract 1C05, 284 (2003).
21. G.G. Amatucci et al., *Solid State Ionics*, **83**, 167-173 (1996).